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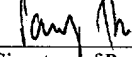
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## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In Re Application of:

Craig J. HAWKER et al.

Group Art Unit: Unassigned

Serial No.: Divisional of 09/261,300

Examiner: Unassigned

Filing Date: Filed on even date herewith

Title: SUBSTRATES PREPARED BY CHEMICAL AMPLIFICATION OF SELF-ASSEMBLED MONOLAYERS WITH SPATIALLY LOCALIZED POLYMER BRUSHES (as amended herein)

### PRELIMINARY AMENDMENT

Box Patent Application  
Commissioner for Patents  
Washington, D.C. 20231

Sir:

This is a preliminary amendment to the patent application identified above, a divisional of U.S. Serial No. 09/261,300, now allowed. Applicants respectfully request entry and consideration of the present amendments prior to examination of the subject application.

### APPENDICES

Appendix A: Amendment to page 1 of the specification.

Appendix B: Pages 24 and 35 of the specification, indicating corrections made.

Appendix C: Corrected pages 24 and 25 of the specification.

Appendix D: Amendments to the title and claims.

Appendix E: Pending claims after entry of this amendment.

Appendix F: Figure 1 as filed with requested amendments indicated in red.

Appendix G: Figure 1 as amended.

## AMENDMENTS

### IN THE TITLE:

Please amend the title of the application to read --SUBSTRATES PREPARED BY  
CHEMICAL AMPLIFICATION OF SELF-ASSEMBLED MONOLAYERS WITH SPATIALLY  
LOCALIZED POLYMER BRUSHES--.

### IN THE SPECIFICATION:

On page 1 of the application, between lines 6 and 8 (immediate prior to the section entitled  
"TECHNICAL FIELD"), please add the new section indicated in Appendix A. The new section  
reads as follows:

#### --CROSS-REFERENCE TO RELATED APPLICATIONS

This is a divisional of U.S. Patent Application Serial No. 09/261,300, filed March 2, 1999.--

Please amend pages 24 and 35 of the specification as indicated in Appendix B. The  
replacement pages with all corrections made are included as Appendix C.

### IN THE CLAIMS:

As requested in Appendix D, please cancel claims 1-23 and amend claims 24 and 25. The  
amended claims read as follows:

24. (Amended) A substrate having a patterned surface, comprising:

- (a) a substrate having a surface with first regions that correspond to a desired surface pattern and  
second regions that correspond to the inverse of the desired surface pattern;
- (b) a first self-assembled monolayer of a first molecular moiety covalently bound to the surface  
within the first regions; and
- (c) a polymeric overlayer comprised of a polymer bound to the first molecular moiety.

25. (Amended) The substrate of claim 24, further comprising: (d) a second self-assembled monolayer of a second molecular moiety bound to the surface in the second regions.

Also add claims 30-39 as indicated in Appendix D. The new claims are reproduced below:

30. The substrate of claim 24, wherein a molecular moiety -A-B is bound to the surface within the second regions, wherein A is a linking group and B is an inert molecular segment.

31. The substrate of claim 30, wherein the molecular moiety -A-B forms a second self-assembled monolayer.

31. The substrate of claim 30, wherein B is hydrocarbyl of 1 to 20 carbon atoms containing 0 to 6 ether linkages.

32. The substrate of claim 31, wherein B is saturated alkyl containing 1 to 15 carbon atoms and 0 to 4 ether linkages.

33. The substrate of claim 31, wherein the molecular moiety -A-B is provided by reaction of the surface with a reactant having the structure A-B, in which A is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl.

34. The substrate of claim 32, wherein the molecular moiety -A-B is provided by reaction of the surface with a reactant having the structure A-B, in which A is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl.

35. The substrate of claim 24, wherein the first molecular moiety has the structure -A'-L-C wherein A' is a surface binding moiety, L is a linker, and C is a molecular segment terminating in a functional group that in turn binds to said polymer.

36. The substrate of claim 35, wherein:

A' is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl;

L is hydrocarbylene of 1 to 20 carbon atoms containing 0 to 6 ether linkages; and

C is selected from the group consisting of -OH, -NH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, alkoxyamine, azo, peroxide, halide and sulfonyl halide.

37. The substrate of claim 36, wherein L is saturated alkylene containing 1 to 15 carbon atoms and 0 to 4 ether linkages.

38. The substrate of claim 24, wherein the second regions have been treated with an etching reagent.

39. The substrate of claim 24, wherein the polymeric overlayer is comprised of a polymer prepared by polymerization of monomers selected from the group consisting of vinyl monomers and cyclic esters.--

For the Examiner's convenience, all claims pending upon entry of this amendment are set forth in Appendix E.

**IN THE DRAWINGS:**

Please amend Figure 1 to replace "SMA" with --SAM-- as indicated in Appendix F.

Also amend Figure 1 to insert the numeral **24** and corresponding arrow as indicated in Appendix F.

The corrected figure is attached as Appendix G.

### REMARKS

The amendment to page 1 of the specification, set forth in Appendix A, identifies this application as a divisional of parent application Serial No. 09/261,300, filed March 2, 1999.

The amendments to the specification set forth on the redacted pages in Appendix B correct a minor and inadvertent spelling error. The misspelled abbreviation "SMA" for "self-assembled monolayer" has been corrected to "SAM" on pages 24 and 35. The corrected pages are included in Appendix C.

Figure 1 has been amended similarly, i.e., to correct the misspelled abbreviation "SMA," as may be seen in Appendix F. As also indicated in Appendix F, Figure 1 has additionally been amended to insert the numeral **24** and corresponding arrow indicating the derivatized surface provided by Step A, microcontact printing. This amendment corrects an inadvertent omission on the original figure, and support for the correction may be found in the specification on page 17, at lines 14-15. The amended figure is included as Appendix G.

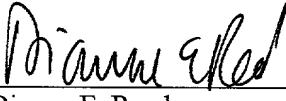
The amendment to the title in Appendix D reflects the focus of this divisional patent application on substrates that have a spatially localized polymer brush thereon, prepared by chemical amplification of an underlying self-assembled monolayer. Support for the new title may be found throughout the original disclosure. The specific terms "spatially localized polymer brush" and "chemical amplification of self-assembled monolayers" find support on page 8, lines 11-12.

The amendments to the claims indicated in Appendix D also clarify the focus of this divisional patent application. The amended and new claims are directed to substrates having a patterned surface with first regions that correspond to a desired surface pattern and second regions that correspond to the inverse of the desired surface pattern, a self-assembled monolayer of a first molecular moiety covalently bound to the surface within the first regions, and a polymeric overlayer comprised of a polymer bound to the first molecular moiety. Minor changes have been made to independent claim 24 that do not change the substance of the claimed subject matter in any way, but are merely semantic and stylistic changes.

New claims 30-39 complement the method claims that have been allowed in the parent application, and contain the same terminology.

If the Office has any questions concerning this communication, please contact the undersigned attorney at (650) 330-0900.

Respectfully submitted,

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APPENDIX A

IN THE SPECIFICATION:

Amend the specification on page 1, by inserting the following new section between lines 6 and 8 (i.e., immediately prior to the section entitled "TECHNICAL FIELD"):

--CROSS-REFERENCE TO RELATED APPLICATIONS

This is a divisional of U.S. Patent Application Serial No. 09/261,300, filed March 2, 1999.--

**APPENDIX B**

**REDACTED PAGES 24 AND 35, INDICATING AMENDMENTS MADE**

Note that in the following amended pages, text to be added is underlined and highlighted, and text to be deleted is crossed out and highlighted, appearing as ~~deleted text~~.



Figure 2, stamp 38 is brought into contact with the surface 46 of substrate 48 in order to transfer the molecular moiety A'-L-C thereto. The pattern 50 of the resultant self-assembled monolayer is thus identical to the pattern of the stamping surface 40; the remaining regions 52 of the conductive surface remain uncovered. In the next step, illustrated as Step B in Figure 2, the exposed functional groups 54 of the self-assembled monolayer are used to attach a polymer or to serve as the initiation site for polymerization, whereby a pattern 56 of brush polymer regions 58 is provided. As illustrated in Step C of Figure 2, the modified surface so prepared is then contacted with an etchant so as to etch away those portions of the conductive substrate surface that are not covered with the polymer-coated SMA-SAM layer, resulting in etched substrate 60. Finally, the organic material is removed from the substrate surface, giving rise to the final product 62.

The present process is also useful in the fabrication of biosensors, high-density assay plates, and the like. Methods for implementation of the presently disclosed and claimed methods in such areas will be readily apparent to those skilled in the art, based upon the present disclosure as well as the pertinent texts, literature references and patents, e.g., U.S. Patent No. 5,512,131 to Kumar et al., cited earlier herein.

For example, biosensors may be fabricated by providing a patterned SAM functionalized with an overlying polymeric brush covalently bound thereto, wherein the "free" termini of the brush polymers have exposed functionalities that are useful in detecting a particular species in a medium. For example, the brush polymers may be provided with an exposed functionality including an antigen, antibody, or any of a variety of specific or non-specific binding pairs. Accordingly, the surface-modified substrate may serve a function analogous to that of a

METHOD FOR FORMING POLYMER BRUSH PATTERN  
ON A SUBSTRATE SURFACE

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ABSTRACT OF THE DISCLOSURE

A method is disclosed for providing a patterned surface wherein predetermined regions of the surface are masked with a self-assembled monolayer ("SMASAM") covalently bound to a brush polymer overlayer. The remainder of the substrate surface will generally be functionalized with a second self-assembled monolayer. Preferably, the method involves a microcontact printing technique, wherein a molecular moiety capable of spontaneously forming an SMA SAM upon transfer to a surface is "stamped" onto a substrate surface, followed by growth (or covalent attachment) of a polymer on exposed functional groups within the SMA SAM molecules. Coverage of surface regions with both an SMA SAM and a polymer overlayer provides a number of advantages, particularly with regard to surface masking during etching and the like. The method is useful in the manufacture of microelectronic circuitry, biosensors, high-density assay plates, and the like.

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**APPENDIX C**  
**REPLACEMENT PAGES 24 AND 35**

Figure 2, stamp 38 is brought into contact with the surface 46 of substrate 48 in order to transfer the molecular moiety A'-L-C thereto. The pattern 50 of the resultant self-assembled monolayer is thus identical to the pattern of the stamping surface 40; the remaining regions 52 of the conductive surface remain uncovered. In the next step, illustrated as Step B in Figure 2, the exposed functional groups 54 of the self-assembled monolayer are used to attach a polymer or to serve as the initiation site for polymerization, whereby a pattern 56 of brush polymer regions 58 is provided. As illustrated in Step C of Figure 2, the modified surface so prepared is then contacted with an etchant so as to etch away those portions of the conductive substrate surface that are not covered with the polymer-coated SAM layer, resulting in etched substrate 60. Finally, the organic material is removed from the substrate surface, giving rise to the final product 62.

The present process is also useful in the fabrication of biosensors, high-density assay plates, and the like. Methods for implementation of the presently disclosed and claimed methods in such areas will be readily apparent to those skilled in the art, based upon the present disclosure as well as the pertinent texts, literature references and patents, e.g., U.S. Patent No. 5,512,131 to Kumar et al., cited earlier herein.

For example, biosensors may be fabricated by providing a patterned SAM functionalized with an overlying polymeric brush covalently bound thereto, wherein the "free" termini of the brush polymers have exposed functionalities that are useful in detecting a particular species in a medium. For example, the brush polymers may be provided with an exposed functionality including an antigen, antibody, or any of a variety of specific or non-specific binding pairs. Accordingly, the surface-modified substrate may serve a function analogous to that of a

METHOD FOR FORMING POLYMER BRUSH PATTERN  
ON A SUBSTRATE SURFACE

5

ABSTRACT OF THE DISCLOSURE

A method is disclosed for providing a patterned surface wherein predetermined regions of the surface are masked with a self-assembled monolayer ("SAM") covalently bound to a brush polymer overlayer. The remainder of the substrate surface will generally be functionalized with a second self-assembled monolayer. Preferably, the method involves a microcontact printing technique, wherein a molecular moiety capable of spontaneously forming an SAM upon transfer to a surface is "stamped" onto a substrate surface, followed by growth (or covalent attachment) of a polymer on exposed functional groups within the SAM molecules. Coverage of surface regions with both an SAM and a polymer overlayer provides a number of advantages, particularly with regard to surface masking during etching and the like. The method is useful in the manufacture of microelectronic circuitry, biosensors, high-density assay plates, and the like.

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**APPENDIX D**

**AMENDMENTS TO THE TITLE AND CLAIMS**

**IN THE TITLE:**

Please change the title of the application from "METHOD FOR FORMING POLYMER BRUSH PATTERN ON A SUBSTRATE SURFACE" to -- SUBSTRATES PREPARED BY CHEMICAL AMPLIFICATION OF SELF-ASSEMBLED MONOLAYERS WITH SPATIALLY LOCALIZED POLYMER BRUSHES.--

**IN THE CLAIMS:**

Please cancel claims 1-23 without prejudice.

Amend claims 24 and 25 as follows:

24. (Amended) A substrate having a patterned surface, comprising:

- (a) a substrate having a surface with ~~predetermined-first~~ regions that correspond to a desired surface pattern and ~~remaining-second~~ regions that correspond to the inverse of the desired surface pattern;
- (b) a first self-assembled monolayer of a first molecular moiety covalently bound to the surface within the ~~predetermined-first~~ regions; and
- (c) a polymeric overlayer comprised of a polymer bound to the first molecular moiety.

25. The substrate of claim 24, further comprising: (d) a second self-assembled monolayer of a second molecular moiety bound to the surface in the ~~remaining-second~~ regions.

Add the following new claims:

30. The substrate of claim 24, wherein a molecular moiety -A-B is bound to the surface within the second regions, wherein A is a linking group and B is an inert molecular segment.

31. The substrate of claim 30, wherein the molecular moiety -A-B forms a second self-assembled monolayer.

32 ~~31~~. The substrate of claim 30, wherein B is hydrocarbyl of 1 to 20 carbon atoms containing 0 to 6 ether linkages.

33 ~~32~~. The substrate of claim 31, wherein B is saturated alkyl containing 1 to 15 carbon atoms and 0 to 4 ether linkages.

34 ~~33~~. The substrate of claim 31, wherein the molecular moiety -A-B is provided by reaction of the surface with a reactant having the structure A-B, in which A is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl.

35 ~~34~~. The substrate of claim 32, wherein the molecular moiety -A-B is provided by reaction of the surface with a reactant having the structure A-B, in which A is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl.

36 ~~35~~. The substrate of claim 24, wherein the first molecular moiety has the structure -A'-L-C wherein A' is a surface binding moiety, L is a linker, and C is a molecular segment terminating in a functional group that in turn binds to said polymer.

37 ~~36~~. The substrate of claim 35, wherein:

A' is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl;

L is hydrocarbylene of 1 to 20 carbon atoms containing 0 to 6 ether linkages; and

C is selected from the group consisting of -OH, -NH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, alkoxyamine, azo, peroxide, halide and sulfonyl halide.

38 ~~37~~. The substrate of claim 36, wherein L is saturated alkylene containing 1 to 15 carbon atoms and 0 to 4 ether linkages.

39 ~~38~~. The substrate of claim 24, wherein the second regions have been treated with an etching reagent.



39. The substrate of claim 24, wherein the polymeric overlayer is comprised of a polymer prepared by polymerization of monomers selected from the group consisting of vinyl monomers and cyclic esters.

**APPENDIX E**

**PENDING CLAIMS UPON ENTRY OF THIS AMENDMENT**

24. A substrate having a patterned surface, comprising:

- (a) a substrate having a surface with first regions that correspond to a desired surface pattern and second regions that correspond to the inverse of the desired surface pattern;
- (b) a first self-assembled monolayer of a first molecular moiety covalently bound to the surface within the first regions; and
- (c) a polymeric overlayer comprised of a polymer bound to the first molecular moiety.

25. The substrate of claim 24, further comprising: (d) a second self-assembled monolayer of a second molecular moiety bound to the surface in the second regions.

26. The substrate of claim 24, wherein the substrate is metallic.

27. The substrate of claim 24, wherein the substrate is comprised of a metal oxide.

28. The substrate of claim 24, wherein the substrate is silicon-containing.

29. The substrate of claim 24, wherein the substrate is polymeric.

30. The substrate of claim 24, wherein a molecular moiety -A-B is bound to the surface within the second regions, wherein A is a linking group and B is an inert molecular segment.

31. The substrate of claim 30, wherein the molecular moiety -A-B forms a second self-assembled monolayer.

31. The substrate of claim 30, wherein B is hydrocarbyl of 1 to 20 carbon atoms containing 0 to 6 ether linkages.

32. The substrate of claim 31, wherein B is saturated alkyl containing 1 to 15 carbon atoms and 0 to 4 ether linkages.

33. The substrate of claim 31, wherein the molecular moiety -A-B is provided by reaction of the surface with a reactant having the structure A-B, in which A is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl.

34. The substrate of claim 32, wherein the molecular moiety -A-B is provided by reaction of the surface with a reactant having the structure A-B, in which A is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl.

35. The substrate of claim 24, wherein the first molecular moiety has the structure -A'-L-C wherein A' is a surface binding moiety, L is a linker, and C is a molecular segment terminating in a functional group that in turn binds to said polymer.

36. The substrate of claim 35, wherein:

A' is selected from the group consisting of -OH, -SH, -NH<sub>2</sub>, -CONH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, -PO<sub>3</sub>H, -SiCl<sub>3</sub>, -SiR<sub>2</sub>Cl, -SR and -SSR wherein R is alkyl or aryl;

L is hydrocarbylene of 1 to 20 carbon atoms containing 0 to 6 ether linkages; and

C is selected from the group consisting of -OH, -NH<sub>2</sub>, -COOH, -SO<sub>3</sub>H, -CN, alkoxyamine, azo, peroxide, halide and sulfonyl halide.

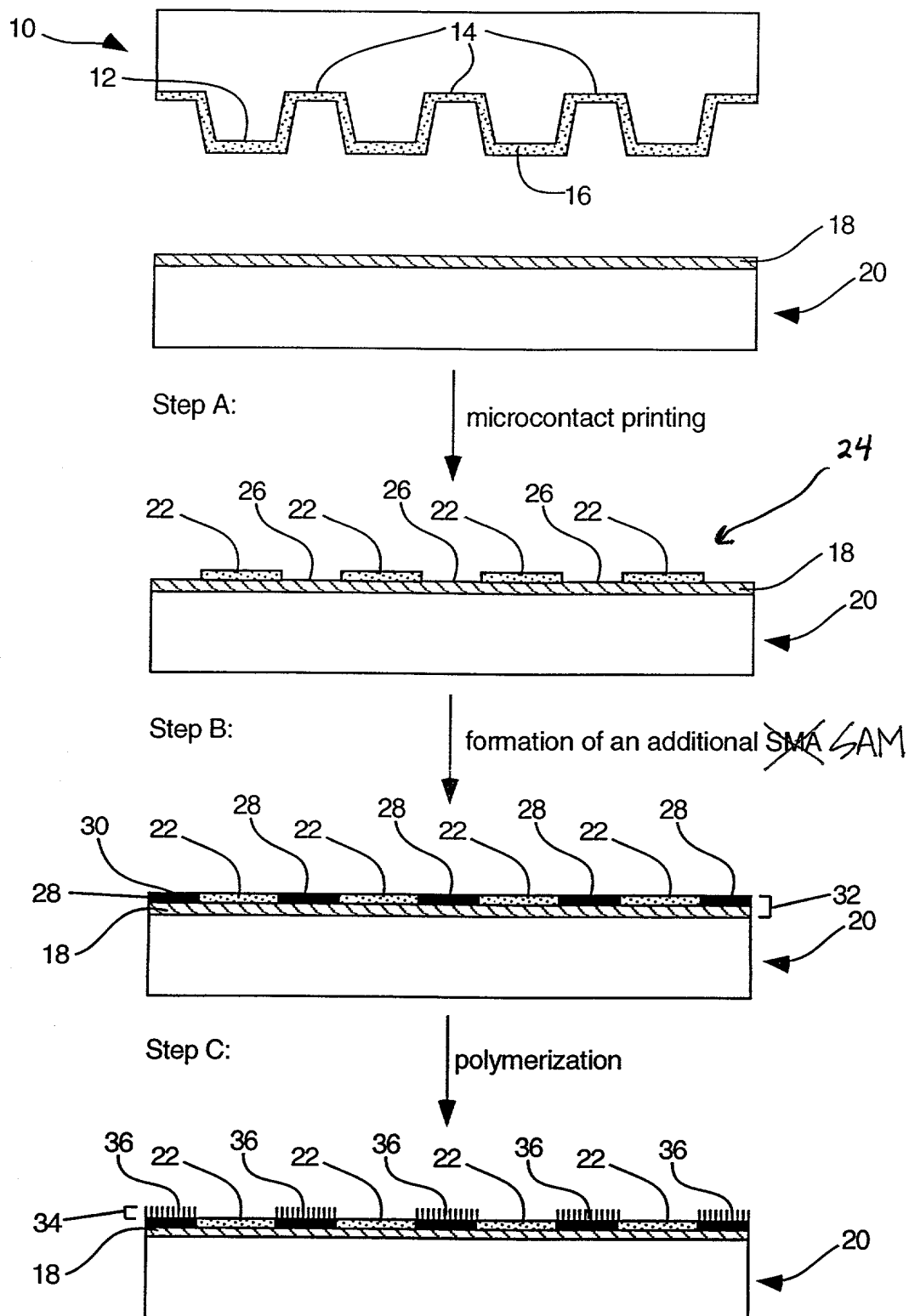
37. The substrate of claim 36, wherein L is saturated alkylene containing 1 to 15 carbon atoms and 0 to 4 ether linkages.

38. The substrate of claim 24, wherein the second regions have been treated with an etching reagent.

39. The substrate of claim 24, wherein the polymeric overlayer is comprised of a polymer prepared by polymerization of monomers selected from the group consisting of vinyl monomers and cyclic esters.

**APPENDIX F**  
**AMENDMENT TO FIGURE 1**

Figure 1



**APPENDIX G**

**FIGURE 1 AS AMENDED**

Figure 1

